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POLYURETHANE COMPOSITE ELEMENTS (SANDWICH ELEMENTS) MANUFACTURED USING RECYCLED POLYOLS, A METHOD FOR MANUFACTURING THEM AND THEIR USE [UNTER EINSATZ VON RECYCLING-POLYOLEN HERGESTELLTE POLYURETHAN-VERBUNDKÖRPER (SANDWICHELEMENTE), EIN VERFAHREN ZU DEREN HERSTELLUNG SOWIE DEREN VERWENDUNG]

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TITLE (54): POLYURETHANE COMPOSITE ELEMENTS (SANDWICH ELEMENTS) MANUFACTURED USING RECYCLED POLYOLS, A METHOD FOR MANUFACTURING THEM AND THEIR USE

FOREIGN TITLE [54A]: UNTER EINSATZ VON RECYCLING-POLYOLEN HERGESTELLTE POLYURETHAN-VERBUNDKÖRPER (SANDWICH-ELEMENTE), EIN VERFAHREN ZU DEREN HERSTELLUNG SOWIE DEREN VERWENDUNG

Description /1*

The invention relates to polyurethane composite elements (sandwich elements) that are manufactured using recycled polyols, a method for manufacturing them and their use in vehicle, furniture, machine and equipment building.

Composite elements with a polyurethane core and fiber-reinforced cover layers of a different material are used in many areas of industry, e.g., for manufacturing high-quality structural components for the passenger car and car body construction, especially the vehicle passenger compartment. Essentially two methods are known in the state of the art for manufacturing this type of sandwich elements. In the depot method (sandwich construction), two half shells are manufactured first, placed in a tool and the cavity between the shells is filled with PUR foam. Also, the shell construction is known, in which a core of a PUR foam is placed in a tool and surrounded with a suitable shell material of, e.g., fiber-reinforced plastics like epoxy resins or unsaturated polyester resins.

To date polyol compounds recovered from polyurethane or polycarbamide waste have hardly been used in the manufacturing of sandwich elements with a polyurethane core.

Thus the object existed of making available a method for manufacturing composite elements with a polyurethane core, in which polyol compounds recovered from polyurethane or polycarbamide wastes can be used.

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*Numbers in the margin indicate pagination in the foreign text.

It has now been found that high-quality composite elements can be obtained, even with polyol compounds recovered from polyurethane or polycarbamide wastes, if these polyol compounds that are used meet certain specifications and are used with cover layers that are reinforced with natural fibers.

Thus the object of the invention is composite elements with a polyurethane core and at least one cover layer of a fiber-reinforced plastic material, whereby the composite element contains

a) a polyurethane core from the chemical reaction of polyisocyanates with polyol compounds obtained by chemical decomposition of polyurethane and/or polycarbamide wastes with an OH index in the range from 100 to 500 mg KOH/g, a water content of 0 to 5 weight-% and a viscosity of more than 2000 mPa.s (20°C) and

b) at least one cover layer of plastic material reinforced with natural fibers.

It is surprising that it is possible at all to manufacture high-quality polyurethane cores for sandwich elements with polyol compounds with this specification, since according to the previously known state of the art, polyols with a far higher OH index, usually in the range of 300 to 1000 and a significantly lower viscosity, usually in the range of < 2000 mPa.s (20°C) had to be used. This specification is always achieved in that the recycled polyols obtained by chemical decomposition of polyurethane or polycarbamide wastes are adjusted to the specification given using the additives named below.

The composite element is present as a sandwich component, which in addition to a polyurethane core on the basis of recycled polyols contains at least one other cover layer of a plastic material, preferably epoxy resins or unsaturated polyester resins reinforced with natural fibers. Preferably the cover layer consists of fiber-reinforced plastic material. In this case, all known fibrous natural fibers can be considered, especially banana, flax, jute, hemp, sisal or coconut fibers in the form of matted fiber, meshes, knits or woven fabrics. These fiber materials can be reinforced with epoxy-unsaturated polyester, PUR, melamine, vinyl resins or also thermoplastic powders. These binders can be applied and incorporated by spraying, rolling, doctor blade or casting and in the case of the preferable use of PUR resins, can also contain PUR recyclates.

Advantageously, the composite elements according to the invention in sandwich construction consist of a cover or shell layer A, consisting of natural fiber reinforced plastic material, a core layer B consisting of polyurethane foam based on recycled polyols and if desired of another layer that is either structured like layer A or can consist of another material. Decorative materials like films, firing skins, textiles or carpet can then be pressed, in a separate work step or even in a single manufacturing step (one step method), directly on the outer surfaces of the cover layers in a known way (direct lamination). With multi-layer sandwich components, additional layers of other materials can also be used if necessary.

All the usual reaction products from the reaction of an isocyanate and the usual diols and/or polyols, e.g. polyesters or polyethers, can be used as polyurethane and/or polycarbamide wastes for manufacturing the polyol compounds used.

Another object of the invention is a method for manufacturing composite elements (sandwich elements) with a polyurethane core and at least one fiber-reinforced cover layer by reaction of polyisocyanates with polyol compounds and possibly other auxiliary materials and additives, in which polyol compounds with an OH index in the range /2 from 100 to 500, preferably 200 to 450 and especially 250 to 400, a water content of 0 to 5 weight-%, preferably 0.2 to 2 weight-% and especially 0.5 to 1 weight-% and a viscosity at 20°C of more than 2000 mPa.s, preferably 3000 to 20,000 mPa.s, and especially 5,000 to 10,000 obtained by chemical decomposition of polyurethane and/or polycarbamide wastes are used for manufacturing the polyurethane core and at least one cover layer of plastic material reinforced with natural fibers in sandwich construction on this polyurethane core.

In the method according to the invention, all known auxiliary materials and additives can be used, e.g., parting compounds, propellants, fillers, catalysts and flame retarding agents.

The method according to the invention can be set up either as a depot or shell construction process. Both the depot construction and the shell construction are known. In the depot process, (filling construction), two half shells (e.g., cover layers of plastics reinforced with natural fiber) are manufactured, placed in a tool and

the hollow space between the shells is filled with the PUR foam according to the invention. In the shell construction, a core of PUR foam according to the invention can be placed in a tool and then covered with natural fiber reinforced shell material, e.g. with natural fiber reinforced epoxy resins or polyester resins.

Preferably the composite elements according to the invention can be manufactured with a foamed PUR core according to the shell construction method with the use of the recycling polyol compounds. To do this, all the usual propellants and auxiliary materials, e.g. parting agents, can be used as desired. If no external parting agent is used in the molding tool during manufacturing according to the invention of a PUR sandwich molded element using the shell construction method, an especially well-adhering bond will be achieved between core and shell material without the necessity of reworking or prior preparation of shell and/or core layer. In this case, all known natural fiber reinforced plastic materials can be used as the shell layer.

The polyols used in the method according to the invention can be obtained from any polyurethane and/or polycarbamide wastes, e.g., also from polyurethane and/or polycarbamide composites by chemical decomposition. These composite substances can consist of PUR and other materials, e.g., thermoplastics, whereby the non-PUR material has to be largely removed before the PUR recycling. A composite material such as this can consist, e.g., of a motor vehicle instrument panel made of a glass-mat reinforced PUR substrate, a soft-to-the-touch PUR foam as

filler material or an aliphatic PUR skin as decorative and covering layer.

The methods for chemical decomposition of polyurethane and/or polycarbamide wastes into polyol compounds are all known. This means polyurethane and/or polycarbamide wastes can be obtained using e.g. aminolysis, alcoholysis or glycolysis methods. Methods of this type have already been described in detail according to the state of the art (e.g. in W. Raßhofer, Recycling of Polyurethane Plastics, Hütig-Verlag, Heidelberg 1994).

Preferably the polyol compounds of polyurethane and/or polycarbamide wastes are obtained in a known way using glycolysis. To do this, coarsely ground or finely crushed polyurethane or polycarbamide wastes are reacted at temperatures of 160 to 240°C with glycols, preferably diethylene glycol, in a weight ratio waste:glycol from 10:1 to 1:2 and preferably 5:1 to 1:1. After a stirring time of approx. 0.5 to 10 hours, a liquid product with the following specifications is obtained: OH index in the range from 20 to 1070, water content in the range from 0 to 5 weight-%, viscosity at 20°C in the range of > 2000 mPa.s. With very high OH indices, the viscosity can also lie under 2000 mPas (20°C).

Since the processing properties of the polyol compounds obtained by chemical decomposition of polyurethane and/or polycarbamide wastes are usually not appropriate for industrial manufacturing of polyurethane composite elements, the specification given is usually adjusted by the admixture of additives. Usually mixtures of known

additive are used for this, like cross-linkers, cell stabilizers, flow agents, parting compounds, catalysts, propellants, etc. in a quantity ratio of 2 to 50 weight-% related to the reaction mixture of recycled polyol compounds used. The additional mixtures usually have OH indices of 300 to 1050 mg KOH/g, viscosities of 100 to 5000 mPa.s, a water content of 0 to 10 weight-% and acid numbers of 0 to 100 mg KOH/g.

It is surprising that polyols with the given specification obtained by chemical decomposition of polyurethane and/or polycarbamide wastes are suitable at all for manufacturing high-quality polyurethane composite elements with sandwich structure since usually when new material is used, the polyols used have to have a significantly higher OH index in the range of over 500 to 1000. Also the viscosity of the polyol compounds used according to the state of the art usually lies significantly lower, at least in the viscosity range of < 2000 mPa.s (20°C). The fact that polyol compounds obtained from polyurethane and/or polycarbamide wastes can be processed to make high-quality polyurethane composite elements in spite of their higher viscosity and their lower activity because of lower OH index was thus unexpected. The polyurethane composite elements according to the invention allow the manufacturing of high-quality structural components for all different types of application areas and permit the use of recycled materials from waste while maintaining the /3 mechanical properties.

The polyols obtained from chemical decomposition of the polyurethane and/or polycarbamide wastes can be reacted with all known

polyisocyanates. For example, aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates can be used as polyisocyanates as are described e.g. by W. Siefgen in Justus Liebigs Annalen der Chemie [Annals of Chemistry], 362, pages 75 to 136, especially those of the general formula

$$Q(NCO)_n$$

in which

n is 2 to 5, and preferably 2 to 3, and

Q is an aliphatic hydrocarbon radical with 2 to 18, and preferably 6 to 10, carbon atoms; a cycloaliphatic hydrocarbon radical with 4 to 15, and preferably 5 to 10, carbon atoms; an aromatic hydrocarbon radical with 6 to 15, and preferably 6 to 13, carbon atoms; e.g. such polyisocyanates as are described in DE-OS 2 832 253, pages 10 to 11.

Especially preferably, the polyisocyanates that are easily accessible technically, e.g., 2,4- and 2,6- toluylene diisocyanate, and any mixture of these isomers ("TDI"), diphenylmethane diisocyanate ("MDI") and polyphenyl polymethylene polyisocyanate, as are manufactured by aniline formaldehyde condensation and subsequent phosgenation and polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, resin groups or biuret groups ("modified polyisocyanates"), especially those modified polyisocyanates that derive from 2,4- and/or 2,6-toluylene diisocyanate and/or 4,4'- and/or 2,4'-diphenylmethane diisocyanate are used.

Another object of the invention is the use of the polyurethane composite elements (sandwich elements) in vehicle, furniture, machine and equipment building. Preferably the polyurethane composite elements according to the invention are used in passenger vehicle construction, especially in motor vehicle passenger compartments. In addition to a low weight with high strength, the sandwich components according to the invention distinguish themselves in that they have an especially low content of emitted and extractable substances because of the use of polyurethane material as the core and natural fiber reinforced cover layer matrix binding material. In the motor vehicle area, they can be used as, e.g., 2 or 3-dimensional molded elements, e.g., as trim parts or covers that can be laminated, inner door trims, brackets, instrument panel holders, air ducts, cable covers, cable conduits and luggage compartment trim. In addition, they can be processed to make housings and housing covers, pallets, small load bearing elements, lids, vertical and horizontal structural components, firewalls, shelves, etc. Also in the area of furniture, the polyurethane molded element according to the invention can be used, e.g., as a substitute for tropical wood, especially in the form of imitation laminated wood manufactured of this.

The following examples will explain the invention, but without limiting its scope.

Examples

Example 1

Chemical decomposition of polyurethane wastes using glycolysis

A granulate with maximum grain size of 8 mm of glass fiber reinforced polyurethane resin with density 1.26 g/cm^3 was subjected to glycolysis. To do this, 4 kg diethylene glycol was measured into a 20 l surface grinding cup equipped with stirrer and heating shroud, covered with nitrogen and preheated to 220°C. Into the hot mixture, 8 kg polyurethane resin granulate was added in portions under nitrogen cover. The addition was measured in such a way that a mixture that could be stirred was present at all times. After complete addition of the granulate, stirring was continued for 90 min at 200-210°C, cooling to 160°C followed and then mixing with 0.2 kg acetic acid ester, followed by stirring for 1 hour at this temperature. A 2-phase product that is liquid when standing is obtained from recycled polyols with the following data:

OH index = 353 KOH/g

NH index = 33 mg KOH/g

Acid number = 0.07 mg KOH/g

Viscosity = approx. 20,000 mPa.s (20°C)

Example 2

Manufacturing of a foamed polyurethane core for a composite element according to the invention.

The recycled polyols obtained in Example 1 by glycolysis were mixed with an additive mixture having the following specification:

OH index = 400 mg KOH/g

Water content = 2.6 %

Viscosity = 1500 mPa.s (20°C)

in a quantity of 25 weight-%, related to the total mixture. A polyol formulation with the following specification is obtained:

OH index = approx. 380 mg KOH/g /4

Water content = approx. 1%

Viscosity = approx. 3500 mPa.s

In a known way according to RIM technology, this polyol formulation was reacted with polyisocyanate (raw MDI) to form a foamed polyurethane molded element. In this case, an external parting agent was not used. A polyurethane molded element is obtained with a raw density of 400 kg/m3.

Example 3

Manufacturing of a composite element (sandwich element) according to the invention

Example 3a

First, outside the tool, cocoanut fiber mats with a weight per surface area of 600 g/m^2 were covered and impregnated in a known way with a PUR matrix material (Baypreg® from Bayer AG).

A cover layer manufactured as described above, a polyurethane core, as described in Example 2 and another cover layer were placed on a tool (steel, 120°C, 300 x 300 x 8 mm) and the tool was closed. After 2 minutes at 120°C and a pressure of 50 bar, a sandwich molded part with an adhering bond was removed from the mold.

Example 3b

As described under Example 3a), a composite element according to the invention was manufactured, whereby additionally a known decorative film of PVC/ABS was placed on one of the cover layers used and the tool was closed. After 2 minutes at 120°C and a pressure of 50 bar, a sandwich molded part with an adhering bond with additional decorative layer was removed from the mold.

All the sandwich elements manufactured according to the invention exhibited a very good adhering bond between core and cover layer with good dimensional stability and strength.

Patent Claims

1. Composite element with a polyurethane core and at least one cover layer of a fiber-reinforced plastic material, characterized in that it contains

a) a polyurethane core from the chemical reaction of polyisocyanates with polyol compounds obtained by chemical decomposition of polyurethane and/or polycarbamide wastes having an OH index in the range from 100 to 500 mg KOH/g, a water content of 0 to 5 weight-% and a viscosity of more than 2000 mPa.s (20°C) and

b) at least one cover layer of plastic material reinforced with natural fibers.

2. Composite element according to Claim 1, characterized in that it contains a cover layer of plastic material reinforced with banana, flax, jute, hemp, sisal and/or cocoanut fibers.

3. Composite element according to Claim 1 or 2, characterized in that it contains a cover layer of polyurethane reinforced with natural fibers.

4. Composite element according to one of Claims 1 to 3, characterized in that it contains a foamed polyurethane core.

5. Method for manufacturing composite elements with a polyurethane core and at least one fiber reinforced cover layer by reaction of polyisocyanates with polyol compounds and possibly other auxiliary materials and additives, characterized in that by reaction of polyisocyanates with polyol compounds and possibly other auxiliary materials and additives, in which polyol compounds with an OH index in the range from 100 to 500, preferably 200 to 450 and especially 250 to 400, a water content of 0 to 5 weight-%, preferably 0.2 to 2 weight-% and especially 0.5 to 1 weight-% and a viscosity at 20°C of more than 2000 mPa.s, preferably 3000 to 20,000 mPa.s, and especially 5,000 to 10,000 obtained by chemical decomposition of polyurethane and/or polycarbamide wastes are used for manufacturing the polyurethane core and there is at least one cover layer of plastic material reinforced with natural fibers in sandwich construction on this polyurethane core.

6. Method according to Claim 5, characterized in that polyol compounds are used that are obtained by glycolysis of polyurethane and/or polycarbamide wastes.

7. Use of composite elements according to one of Claims 1 to 4 in vehicle, furniture, machine or equipment building.